REMEDIATION OF CADMIUM AND LEAD IN CONTAMINATED SOIL USING BIOCHAR-PALYGORSKITE COMPOSITE

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Abstract. The biochar-palygorskite composite (BC/PAL) was synthesized and applied in the remediation of soil polluted by heavy metals. The efficiency of BC/PAL on the soil physicochemical property, the bioavailability and chemical fraction of Cd and Pb in the soil, the growth of the plants and heavy metals accumulation in maize (*Zea mays* L.) were investigated by pot and incubation experiments. The data show that BC/PAL can greatly enhance the stability of Cd and Pb, facilitating their transition from labile to stable components. And the composite can also reduce the $CaCl_2$-extractable Cd and Pb with a maximum reduction efficiency of 57.76% and 42.81%, respectively. The fresh weight of corn seedlings had a more than sevenfold increase and the accumulation of Cd and Pb in shoot and root parts decreased significantly. BC/PAL can effectively improve the contents of soil available nutrients, soil enzyme activity, and organic carbon content. It can significantly reduce the bioavailability and ecotoxicity of Cd and Pb in the soil. The biochar-palygorskite composites can be further investigated as an efficient, environmentally friendly, and cheap remediation material for heavy metal contaminated soil.
Keywords: *biochar, palygorskite, heavy metals, immobilization*

Introduction

In recent years, with the development of industry and agriculture, the problem of soil heavy metal pollution in China has become prominent increasingly (Hu et al., 2020; Xu et al., 2020a). Once a heavy metal enters the environment, its removal or biodegradation is difficult while it accumulates in animals and the human body through the food chain affecting human health by the impairment the of immune, nervous and endocrine systems (Hu et al., 2019). The types of heavy metal pollution are mainly Cd, Cu, Zn, Cr, etc. It is usually dominated by a certain heavy metal element pollution, and the soil heavy metal composite pollution in which a variety of other heavy metals coexist (Qin et al., 2021). Interactions exist between various heavy metal elements or compounds in the soil making it challenging to remediate contaminated soils (Derakhshan et al., 2017). At present, soil heavy metal remediation technologies mainly include physical remediation, chemical remediation and bioremediation. In-situ chemical stabilization technology is one of the main technologies of chemical remediation which has the advantages of obvious effect, low cost and environmental friendliness (Wang et al., 2018). It mainly changes the chemical fraction of heavy metals in the soil through adsorption, precipitation, and ion exchange by applying one or more stabilizers to the soil, thereby reducing the biological availability of heavy metals in the contaminated soil (Ning et al., 2016). This remediation method is mainly suitable for large areas of medium and low heavy metal contaminated soils (Yang et al., 2018).

The key to implement in-situ chemical stabilization technology is the selection of stabilizers. Biochar is a highly aromatic and intolerant solid material, which is generated

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from waste biomass through anoxic thermal polymerization. It has the advantages of a large specific surface area, many micro-pores, and good adsorption performance (Jiang et al., 2020; Liu et al., 2020). The effect of biochar on the bioavailability of heavy metals in soil includes direct and indirect effects. The effects of biochar are shown in *Figure 1*. It can not only affect the physical and chemical properties of soil, but also significantly affects the form transformation of heavy metals in soil, thereby reducing the environmental risk of heavy metal contaminations in soil (Munir et al., 2020; Yang et al., 2021). The application of biochar can significantly promote metabolic physiological indicators such as plant biomass, chlorophyll synthesis, photosynthetic parameters, stomatal conductance, and antioxidant enzyme activity. Thereby reducing the toxic stresses such as drought, low temperature, salt and heavy metals.

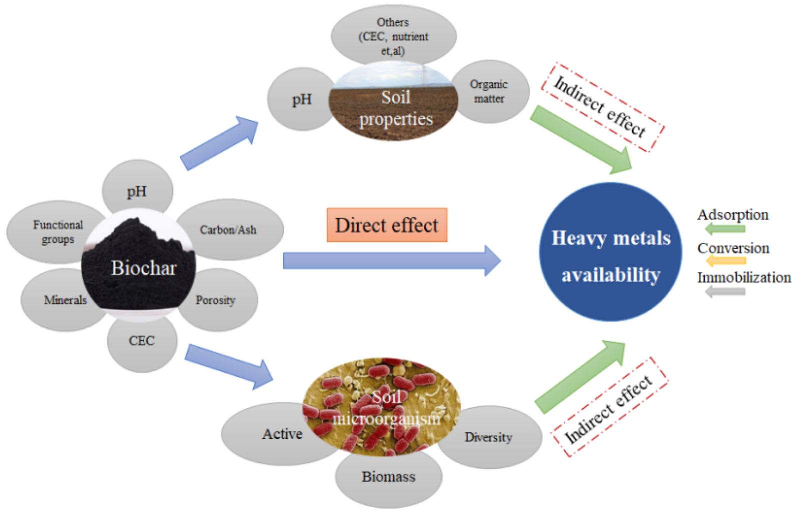

Figure 1. *The effects of biochar on available heavy metals in the contaminated soil*

The output of agricultural straws and rice husks in China is huge, and most of them are left idle or incinerated due to the lack of effective treatment methods, which not only pollutes the environment but also causes great waste. Therefore, agricultural wastes are used as raw materials to prepare the biochar by carbonization and used as a stabilizer, which can not only reduce environmental pollution but also realize the resource utilization of agricultural wastes (Nkoh et al., 2022). Biochar adsorbs heavy metals mainly through physical adsorption, electrostatic interaction, ion exchange and surface complexation, of which ion exchange and surface complexation play a leading role (Mehmood et al., 2018; Mu et al., 2018). In order to reduce the cost of biochar stabilizers and improve the adsorption performance of carbon materials, many scholars have modified biochar. The HNO_3 modified wheat straw biochar has a 40-fold increase in the adsorption capacity of U(VI) compared with the unmodified wheat straw biochar (Jin et al., 2018). It is because HNO_3 modification increases the content of -COOH functional groups on the surface of biochar and reduces the Zeta potential, which promotes the complexation and electrostatic interaction between U(VI) and the surface of biochar. Li et al. reported that attapulgite modified biochar had the potential as a green cost-effective adsorbent for remediating norfloxacin contaminated water environment (Li et al., 2017b). In addition, persistent free radicals in biochar can participate in the redox process of heavy metals, and modification can regulate the type

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and quantity of persistent free radicals in biochar. For example, iron salt modification is beneficial to the development of the degree of graphitization. The persistent free radicals centered on carbon are generated, thereby promoting the transfer of electrons and then reducing Cr(VI) to Cr(III) (Zhong et al., 2018). However, modified biochar has certain environmental risks. The modification process of strong acid or alkali may lead to secondary pollution, and the persistent free radicals generated by transition metal modification may be harmful to human health. Moreover, some studies have also shown that excessive biochar application will inhibit the growth and development of rice and corn. It not only has a strong adsorption effect on heavy metals, but also has a strong adsorption effect on nutrients such as cations in the soil. The excessive application will affect the absorption of nutrients thereby affecting the growth and yield of the plant. It is necessary to combine the application of biochar and other materials to reduce the mobility of soil heavy metals and the uptake of soil heavy metals by crops.

Palygorskite (PAL) is a kind of representative aluminum-magnesium silicate mineral with parallel ribbons of a 2:1 layer structure and its structure is $(Mg,Al,Fe)_5Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ (Liang et al., 2014). The crystals are rod-shaped or fibrous, with pores running through the layer, and the outer surface is uneven. Palygorskite also with a large specific surface area, high thermal stability, good adsorption and ion exchange performance. However, natural palygorskite contains a lot of associated minerals and silicate impurities, which makes it have certain limitations in use (Ren et al., 2020). There are few reports on the preparation of new soil stabilization materials by using the adsorption properties of the two materials at the same time.

In this study, corn stalk and palygorskite were used as raw materials to prepare corn stalk biochar-palygorskite composite materials, and the actual heavy metal composite contaminated soil was stabilized by applying biochar, palygorskite and biochar-palyforskite composite materials respectively. The available content of Cd and Pb before and after stabilization was analyzed. At the same time, the effects of different stabilizers on soil properties were analyzed by measuring soil physicochemical properties and enzyme activities before and after stabilization, to screen out the better stabilizer. This work may synthesize an efficient, cheap and environmentally friendly amendment and provide the technical guidance for soil remediation of heavy metal complex pollution.

Materials and methods

Soil

The heavy metal-contaminated soil selected in this study was collected from farmland soil around Silong Town (36°29′39″N, 104°16′5″E), Baiyin City, Gansu Province. Due to historical reasons, industrial wastewater and domestic sewage were used for irrigation in this area all year round, resulting in serious excess of Cd, Pb, Cu, Zn and other heavy metals in the local farmland soil (Xu et al., 2020b). In particular, the content of Cd in soil was much higher than the level 3 standard (≤1 mg/kg) of soil environmental quality standard (GB15618-1995). According to the survey, the main economic crops currently planted in this area include corn, wheat, celery, green onions, and oil sunflowers.

The surface layer (0-20 cm) soil mixture was collected by the plum blossom sampling method. After collection, impurities such as large stones were removed, then air-dried naturally, and passed through 10-mesh and 100-mesh nylon mesh sieves for use. The pH of the heavy metal-contaminated soil remediated in this study was

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7.01 ± 0.03; the organic carbon content was 13.15 ± 0.22 g/kg; the available nitrogen content is 136.70 ± 9.29 mg/kg; the available phosphorus content is 14.96 ± 1.91 mg/kg; the available potassium content is 113.47 ± 1.74 mg/kg; the total amount of heavy metals Cd and Pb 19.15 ± 0.58 and 94.21 ± 1.46 mg/kg.

Biochar-palygorskite composite

The corn stalk was adopted as the carbonization raw material that was taken from the Gansu Academy of Agricultural Sciences. The palygorskite selected in this study was purchased from Lanzhou Hanxing Environmental Protection Co., Ltd., China. The corn stalk (CS) and palygorskite (PAL) were mixed with different mass ratios (CS:PAL = 2:1, 1:1, 1:2) in the ethanol solution by ultrasonic mixing for half an hour and then stirred for 12 h. After drying at 70°C overnight, the samples were crushed into powder, and the obtained samples were recorded as CP21, CP 22, and CP 12, respectively. The slow oxygen-limited pyrolysis method was used to prepare biochar-palygorskite composites (BC/PAL). A certain amount of CS/PAL was weighed and placed in a porcelain boat, and the temperature was programmed to heat up to 600°C for 2 h at 5°C/min under the N_2 atmosphere. Using 1 mol/L HCl to pickle and remove impurities (Li et al., 2017b). The black particles obtained after washing to neutrality are biochar-palygorskite composites, which are named BP21, BP22, and BP12 according to the mixing ratio of BC and PAL. The BC was prepared under the same conditions without adding the PAL. Then the morphology and surface structure of biochar, palygorskite and biochar-palygorskite composites was measured by a scanning electron microscope (SEM; Zeiss Supra55VP, Germany). The surface functional groups of materials were observed by Fourier transform infrared spectroscopy (FT-IR, VERTEX 70, Germany). The crystal of BC, PAL and biochar-palygorskite composites was determined by X-ray diffraction (XRD, PANalytical Empyrean, Netherlands) under 2° to 80° at a scanning speed of 2° per minute measurement condition.

Experiment design

Place 1.5 kg of contaminated soil in a 2 L plastic pot at room temperature (22-25°C), add distilled water to keep the soil moisture at 70% of the field capacity, and record the initial mass. Fully mix BP21, BP22, BP12, pure PAL and pure BC with the contaminated soil in an amount of 4% (w/w, on an air-dry weight basis), stir evenly and place at room temperature for 30 days and replenish the water every 3 days. The water content of the mixed sample was kept constant by the weighing method. The soil without adding any amendment was regarded as control (CK). Each treatment group were performed in triplicate. After 30 days of incubation, the 200 g soil sample was taken out from each treatment to determine the changes in soil physical and chemical properties and heavy metal contents.

Then 10 corn seeds (*Zea mays* L.) were evenly planted in each pot (25°C), thinning was performed when the second cotyledon grew. Remained 6 seeds in each pot and the plants were harvested after 45 days at seedling stage using scissors (*Fig. 2*). The plastic pots were alternated weekly to ensure randomness in the growing environment (Liu et al., 2018; Yin et al., 2014). The test plants used in this experiment were spring maize (*Zea mays* L.) with a large planting area in northwest China. The variety is “Changchun Zeyu 709”, which was supplied by the Gansu academy of agricultural sciences. The concentrations of Cd and Pb in corn seed were too low to detect by AAS.

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Figure 2. *The photo of the experimental culture*

Sample analysis

The determination of soil heavy metals and physical and chemical properties was performed according to the technical specifications for soil environmental monitoring (HJ/T 166-2004). The bioavailability content of Cd and Pb was extracted by $CaCl_2$, and the ratio of 0.1 mol/L $CaCl_2$ to soil was 25:1 (v:m). After vibration extraction, the heavy metal contents in the filtrate are measured by the atomic absorption spectrometer (AAS, Persee TAS-990, Beijing). The soil pH value was measured by a potentiometric method with a soil-water ratio of 1:2.5 (m:v) using the pH electrode (Leici pH3C, Shanghai) (Mi et al., 2020). Soil available nitrogen was measured by the alkaline hydrolysis diffusion method. Soil available phosphorus content was extracted by sodium bicarbonate-molybdenum-antimony anti-spectrophotometry method. 0.5 mol/L $NaHCO_3$ solution and soil ratio of 20:1 (v:m) shaking extraction, molybdenum antimony anti-color developer was used for color development and colorimetric determination with UV-6000 ultraviolet spectroscopy photometer (ACCURATE, Shanghai). Soil available potassium content was extracted by ammonium acetate extraction-flame photometer method, and the ratio of ammonium acetate solution to soil was 10:1 (v:m) for vibration extraction and measured by flame photometer (FP6410, Shanghai INESA) (Wang et al., 2022). Soil organic carbon is oxidized by the potassium dichromate external heat method. Potassium dichromate standard solution, concentrated sulfuric acid and soil is mixed at 20:20:1 (v:v:m), and boiled in a paraffin oil bath at 170-180°C. After 5 min, the Phen indicator was added and $FeSO_4$ was used to titrate until the color changed. Soil enzyme activities were determined by spectrophotometry (Xu et al., 2020b; Zhai et al., 2018). The BCR (European Community Bureau of Reference) sequential extraction method was used to determine the content of different chemical fractions of heavy metals. This method divides heavy metals into four fractions: acid exchangeable fraction, reducible fraction, oxidizable fraction and residual fraction (Liu et al., 2019; Zhang et al., 2018). The total concentrations of Cd and Pb in soil were measured by AAS after digesting with HNO_3-HCl-$HClO_4$ (v:v:v = 1:3:1) (Mehmood et al., 2018). The concentrations of Cd and Pb in plants were measured by AAS after digesting with HNO_3 and $HClO_4$.

Statistical analysis

The experimental data were organized using Excel 2010, and one-way ANOVA was performed using SPSS 18.0. The Duncan's test was used to compare the significance of differences between treatments ($P < 0.05$), and Origin 9.1 software was used for graphing.

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Results

Characterization of stabilizers

Multiple characterization techniques of FTIR, XRD, and SEM were chosen to illustrate the stabilization mechanisms. The surface functional groups of the stabilizers were analyzed via FTIR (*Fig. 3a*). The broad bands at around 3442 cm^{-1} were assigned to the O-H stretching vibration resulting from iron oxyhydroxide or cellulose (Yang et al., 2020). The peaks at 1643-1612 cm^{-1} were attributed to the C = O stretching and bending vibration caused by CO_2 adsorption. New peaks at about 464-449, 1011 cm^{-1} (except BC) were associated with Si-O-C and Si-O-Si stretching vibrations (Wang et al., 2022). A large number of oxygenic functional groups on biochar-palygorskite composites are conducive to the stable complexation of heavy metals (Li et al., 2020; Liu et al., 2020; Mi et al., 2021). Characteristic peaks of typical amorphous carbon at 2θ = 22° were observed at BC in XRD patterns (*Fig. 3b*), which is similar with other reports (Nkoh et al., 2022). The new diffraction peaks of BP21, BP11 and BP12 were shown at 20.7°, 26.6° and 50.4° which represent the diffraction pattern of SiO_2 and carbonate. The characteristic peaks of both BC and PAL were present in biochar-palygorskite composites which suggested that palygorskite was loaded on the surface of biochar.

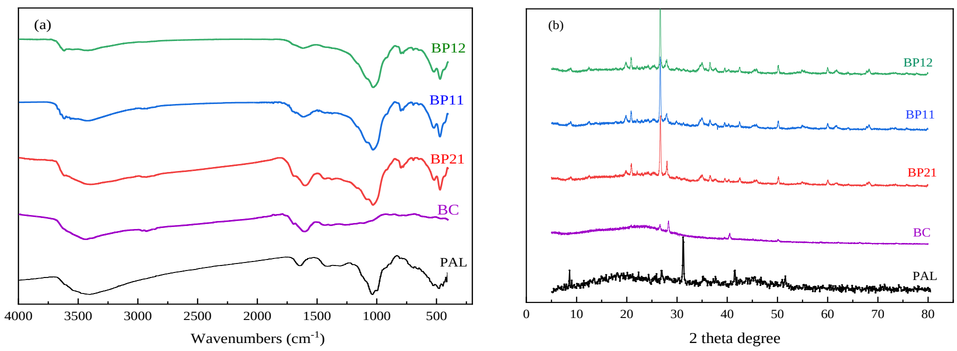

Figure 3. *(a) FT-IR spectra and (b) XRD patterns of BC, PAL, BP21, BP11 and BP12*

Figure 4 show the SEM images of PAL, BC, BP21, BP11 and BP12. Pristine BC existed as an irregular sheet (Wang et al., 2022). After compsite the palygorskite with biochar, PAL grows on the surface of BC uniformly, and this phenomenon was more obvious with the increase of PAL. The modification of biochar by natural clay minerals can effectively increase the specific surface area and pore volume of the material, so as to improve the adsorption performance of the material for heavy metals. The FTIR, XRD and SEM results illustrated that the biochar-palygorskite composites were synthesized successfully.

Physical and chemical properties of soil

Soil pH

After 30 days of the incubation period, the pH value increased significantly after adding different amendments compared with CK, following an order BP11 > BC = BP21 = BP12 > PAL (*Fig. 5*). The value of pH reached 8.07 ± 0.03 when the soil received BP11, which increased the pH by 1 unit over the soil without amendments. Application of BC increased soil pH value more than PAL alone in contaminated soil.

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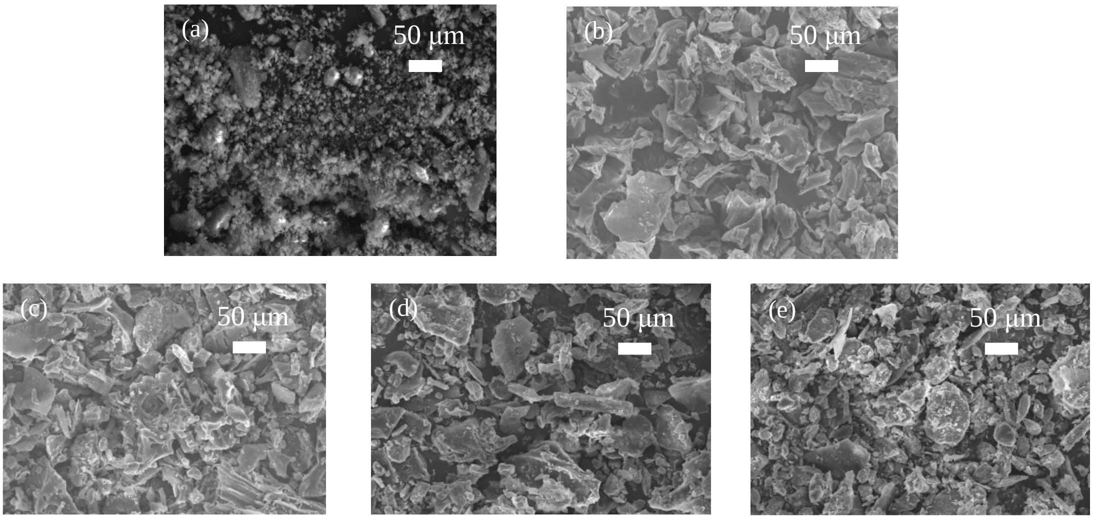

Figure 4. *SEM images of (a) PAL, (b) BC, (c) BP21, (d) BP11, (e) BP12*

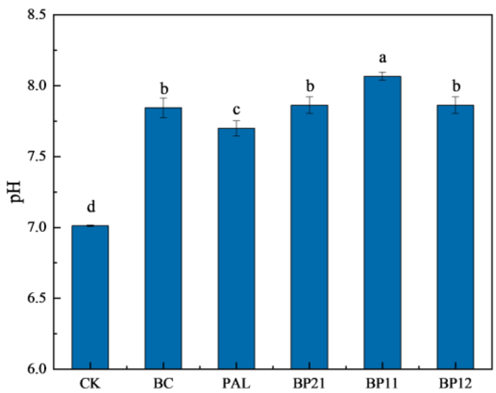

Figure 5. *Effect of stabilizers on soil pH. Data were means ± SD (n = 3). Column with the different letter has significant differences among all treatments at according to the Duncan's test (P < 0.05)*

Soil enzyme activities

The changes of soil enzyme activities were shown in *Figure 6* after adding the different amendments. It can be noted that the biochar-palygorskite composite could improve the urease activity and catalase activity in soil apparently while reducing the acid phosphatase activity slightly. After 30 days of incubation, the soil acid phosphatase activity reduced from 15.11 ± 0.66 to 12.25 ± 0.52 μmol/d/g when treated with palygorskite alone. There were no significant differences in soil acid phosphatase activity after adding BC and BP21 to CK. The soil urease activity showed an upward trend after adding five stabilizers compared with CK. BP11 had the best improvement effect compared with the CK and the urease activity was increased by 9.56%. It showed that the application of biochar-palygorskite composite was beneficial to the hydrolysis of urea by soil urease and promote the absorption of soil nitrogen by plants. After adding the BC, the activity of soil catalase activity showed a downward trend while adding PAL had the opposite trend. After adding the PAL and BP12, the catalase activity increased by 26.53% and 17.53%, respectively compared with CK.

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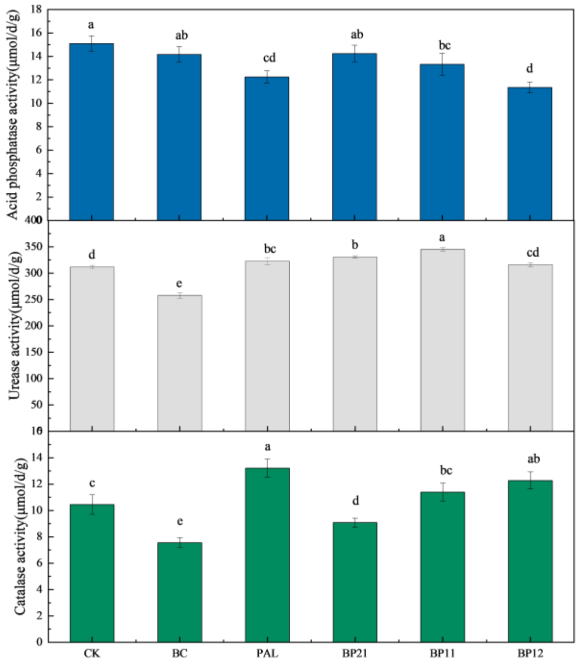

Figure 6. *Effect of stabilizers on enzymatic activity of soil. Data were means ± SD (n = 3). Column with the different letter has significant differences among all treatments at according to the Duncan's test (P < 0.05)*

Available nutrient contents

After 30 days of incubation, the available nutrient contents in the soil had taken place with significant improvements except for the available nitrogen (*Fig. 7)*. The available nitrogen content in the soil did not change significantly compared with the CK, no matter which remediation agent was used. After adding BC and biochar- palygorskite composite, the content of soil available phosphorus increased while decreased slightly after adding palygorskite. The available phosphorus content in soil increased by 57.82% and 56.68% after the treatments of applying BC and BP21 compared with CK. Under the same amount of stabilization material, the content of soil available potassium with BC was higher than that with palygorskite and biochar-palygorskite composite. Compared with CK, the content of available potassium increased by 62.10% and 46.23% after applying BC and BP21.

Organic carbon content

The content of organic carbon in soil with the addition of different amendments in soil was shown in *Figure 8*. Compared with CK, the mean content of soil organic carbon increased from 13.15 ± 0.22 to 29.48 ± 0.56, 25.66 ± 0.69 and 23.28 ± 1.71 g/kg after adding BC, BP21 and BP11, respectively. This is consistent with the findings of Laird et al. that BC can improve the stability of soil aggregates and reduce the loss of soil organic carbon (Laird et al., 2010).

$CaCl_2$-Cd and Pb in soil

The effect of BC, PAL and biochar-palygorskite composite on $CaCl_2$-Cd and Pb in soil was evaluated. As shown in *Figure 9*, after adding biochar-palygorskite composite

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with different mass ratios, the Cd concentration of $CaCl_2$ extract decreased by 51.00%, 57.33% and 57.76% compared with CK after 30 days in the polluted soil, respectively. The Pb concentration of $CaCl_2$ extract also has a significant decrease after applying the different amendments. Applying the biochar-palygorskite composite was more effective in reducing the bioavailability of heavy metal in soil than adding BC and PAL alone. The BP21 showed the best effect with a drop rate of about 42.81% compared with CK.

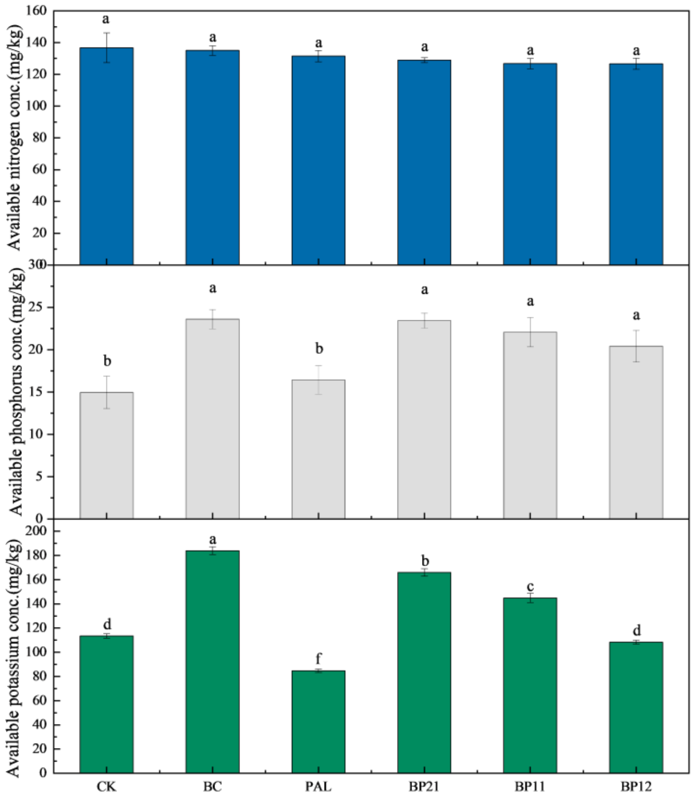

Figure 7. *Effect of stabilizers on available nutrients contents of soil. Data were means ± SD (n = 3). Column with the different letter has significant differences among all treatments at according to the Duncan's test (P < 0.05)*

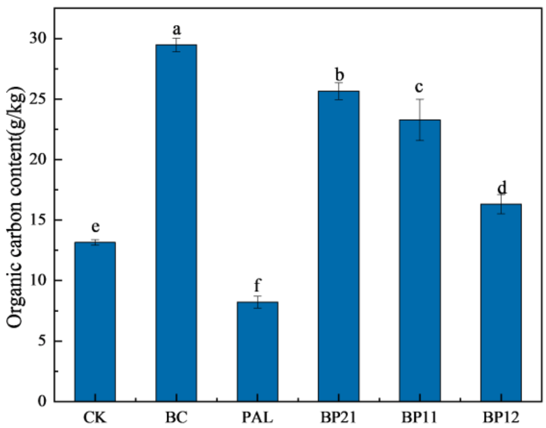

Figure 8. *Effect of stabilizers on organic carbon content of soil. Data were means ± SD (n = 3). Column with the different letter has significant differences among all treatments at according to the Duncan's test (P < 0.05)*

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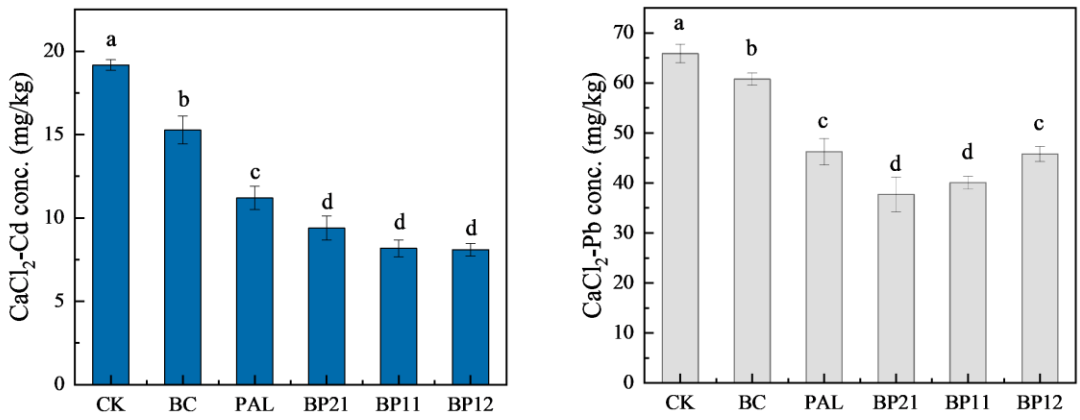

Figure 9. *The $CaCl_2$ -extractable Cd and Pb in the soil treated with various stabilizers. Data were means ± SD (n = 3). Column with the different letter has significant differences among all treatments at according to the Duncan's test (P < 0.05)*

Fractionation of Pb and Cd in soil

Figure 10 shows the change of Cd and Pb chemical fractions in contaminated soil in each remediated sample. After adding BC, PAL and biochar-palygorskite composite with different mass ratios, the various fractions of Cd are transformed into each other. In untreated soil, the fraction of Cd mainly exists in the acid-exchangeable fraction accounting for 65.12% of the total Cd concentration. After the BP11 was added, the acid exchangeable fraction decreased to 40.17% while the residual fraction increased by 23.40% compared with CK. Simultaneously, the chemical fraction of Pb occurred in a manifest transformation. It is different from the Cd in the soil, the Pb mainly occurs in the reducible fraction accounting for 75.17% of the total Pb concentration in the polluted soil. After the amendments were added, the residual fraction significantly increased and the proportion of the other three fractions decreased significantly. When adding the BP21, BP11 and BP12, the reducible fraction decreased by 19.03%, 21.47% and 18.69%, respectively. At the same time, the residual fraction increased by 22.26%, 25.58% and 22.84%, respectively.

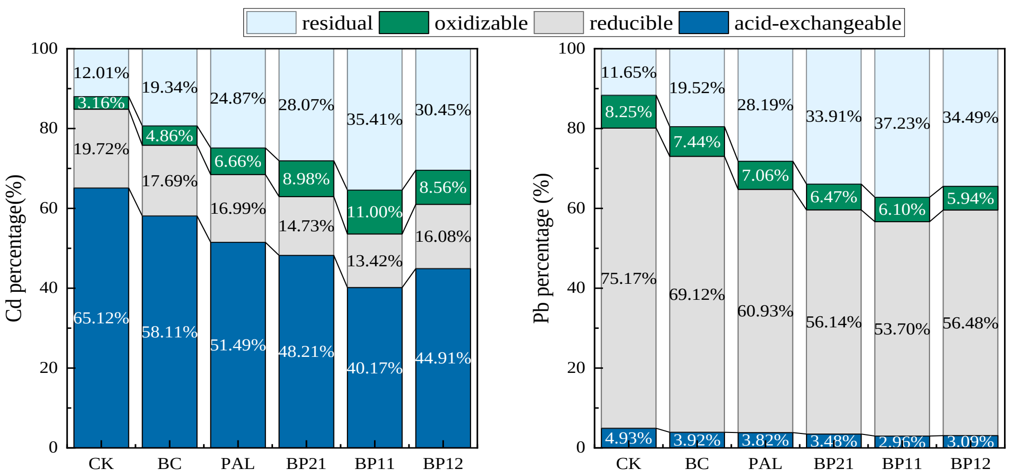

Figure 10. *The fractions of different Cd and Pb speciation in soil treated with various stabilizers*

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Plant biomass and heavy metals accumulation

The pot experiment also was conducted to confirm whether the biochar-palygorskite composites could really mitigate the potential risk from the heavy metals in polluted soil. As shown in *Figure 11*, all stabilizers stimulated the growth of corn distinctly. The fresh weight of corn seedlings had a more than sevenfold increase after adding BP21 and BP11 compared to the treatments without amendments.

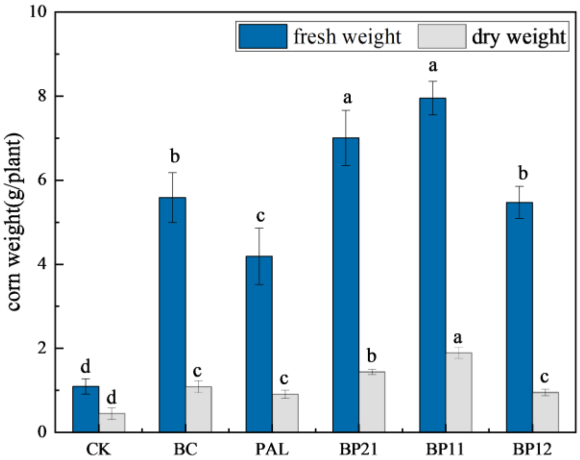

Figure 11. *The corn fresh and dry weight harvested from the soil treated with various stabilizers. Data were means ± SD (n = 3). Column with the different letter has significant differences among all treatments at according to the Duncan's test (P < 0.05)*

Among the three composites (*Fig. 12*)., BP11 was superior in reducing Cd and Pb accumulations in the corn. Compared to the sample without remediation, the concentration of Cd in corn shoot and root decreased by 67.39% and 42.92%, respectively. The concentration of Pb was reduced by 57.15% and 50.60% in corn shoot and root parts, respectively.

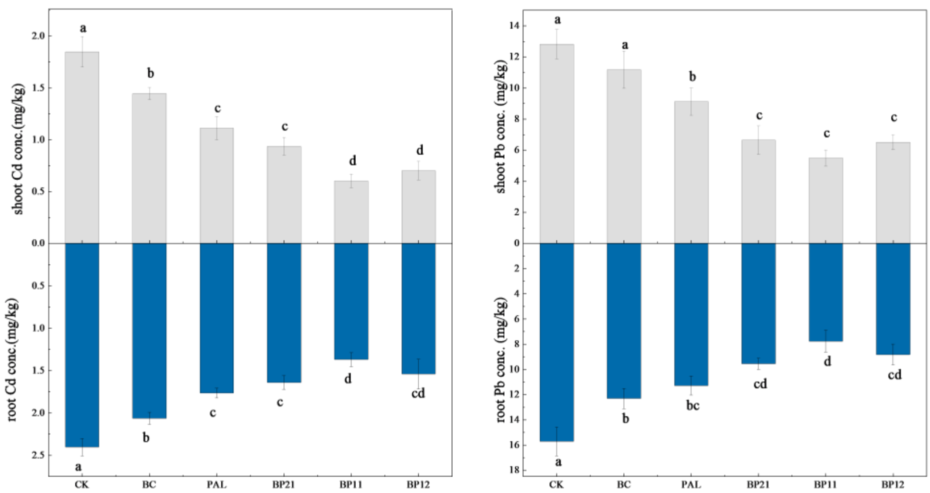

Figure 12. *Concentration of Cd and Pb in corn shoots and roots part harvested from the soil treated with various stabilizers. Data were means ± SD (n = 3). Column with the different letter has significant differences among all treatments at according to the Duncan's test (P < 0.05)*

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Discussion

Change of soil physical and chemical properties

Biochar is usually alkaline or neutral, and the protonation of carboxyl groups on its surface and the dissolution of carbonate are the main reasons for the increase in soil pH (Yu et al., 2019). The raw materials of biochar (especially plants) contain various mineral elements, such as K, Ca, Na, Mg and Si. The alkaline substances, such as carbonate and silicate, will be formed after pyrolysis. Moreover, the negatively charged carboxyl groups, hydroxyl and phenol can also combine with H^+ to further increase the pH of the soil (Gul et al., 2015; Palansooriya et al., 2019). The addition of PAL to the soil will generate soluble silicates (such as calcium, magnesium, etc.) and react with Al^{3+} in the soil to form stable amorphous hydroxy silicates, which will also increase the soil pH value (Mi et al., 2021). When the corn stalk biochar was mixed with palygorskite into the soil system, the soil pH value would be changed dramatically, with BP11 treatment showing the best effect.

Soil enzymes are produced by soil microorganisms, plant roots and their residues, soil animals and their remains (Xu et al., 2020b). They can catalyze the conversion of complex organic matter into simple inorganic matter that is easily absorbed and utilized by plants. Its activity is one of the important factors in evaluating soil fertility and soil quality. Studies have shown that the leachable contents of Cd and Pb were negatively correlated with soil enzyme activity (Hazrati et al., 2021). That is to say, the enzyme activity gradually increased with the decrease of heavy metal content. It indicated that the application of BC inhibited the activity of soil catalase and reduced the ability of soil to decompose hydrogen peroxide, while the application of a certain amount of PAL and biochar-palygorskite composite could promote the activity of soil catalase and accelerate the decomposition of hydrogen peroxide in soil.

Adding a certain amount of BC and biochar-palygorskite composite could observably promote the soil available phosphorus content. It possibly because the biochar could effectively reduce the loss of soil soluble phosphorus. Studies by Laird et al. show that adding 2% biochar to soil can reduce the loss of soil soluble phosphorus by up to 69% (Laird et al., 2010). With the application of BC, a certain amount of potassium was released into the soil, which increased the content of available potassium in the soil. It will be beneficial to the planting and growth of crops. Yuan et al. also pointed out that biochar itself contains phosphorus, potassium and other mineral elements, which can be returned to the soil after application to improve the nutrient content of the soil (Yuan et al., 2011).

Palygorskite is a magnesium aluminosilicate mineral, which is an inorganic substance. Due to the effect of physical dilution action, it will have a significant decrease in the content of soil organic carbon with the increase of the additional amount. Biochar is rich in organic carbon, which can convert easily mineralized and decomposed carbon into complex and stable carbon forms such as phenols and furans during high-temperature carbonization and pyrolysis, to achieve the purpose of long-term carbon sequestration, and can also promote the formation and stabilization of soil aggregates to increase the soil organic matter content (Li et al., 2017a). Under the action of biochar, soil organic matter mainly absorbs heavy metals through the complexation of its own functional groups (carboxyl, hydroxyl, carbonyl, etc.), further influencing the mobility, availability and transformation process of heavy metals in the soil (Ondrasek et al., 2019). However, the application of biochar may increase the content of dissolved

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organic carbon (DOC) in the soil, which can enhance the mobility of heavy metals in the soil by competing for adsorption sites or forming soluble complexes, and even increase the risk posed by heavy metals (Borggaard et al., 2019).

Decrease of $CaCl_2$-Cd and Pb in soil

The process of BC/PAL affecting the bioavailable of Cd and Pb in the soil includes physical and chemical mechanisms. In the process of physical adsorption, BC/PAL mainly enhances the adsorption of heavy metals through van der Waals forces. The larger surface area and good pore structure are conducive to the contact of heavy metals with the adsorption sites on the surface of the stabilizer and are also conducive to their migration and diffusion into the pores. In the process of chemical mechanism, BC/PAL is rich in functional groups (such as -COO(-COOH), -O-(-OH), etc.) and minerals which can directly adsorb heavy metals, mainly including electrostatic attraction, ion exchange, precipitation, complexation, cation-π and other mechanisms.

BC/PAL contains many surface functional groups such as carboxyl, hydroxyl, and amino groups, which can be used as adsorption sites to combine with heavy metals to form surface complexes, reducing the availability of Cd and Pb in soil. The general reaction formula is expressed as follows (M is heavy metals):

$$\text{BC/PAL-OH}+\text{M}^{2+}+\text{H}_2\text{O}\rightarrow\text{BC/PAL-OM}+\text{H}_3\text{O}^+ \tag{Eq.1}$$

(Complex with surface functional groups, taking hydroxyl as an example)

$$2\text{BC/PAL-COOH}+\text{M}^{2+}\rightarrow(\text{BC/PAL-COO})_2+2\text{H}^+ \tag{Eq.2}$$

(Exchange with strongly acidic oxygen-containing functional groups, take carboxyl as an example)

There are Ca^{2+}, Cu^{2+}, Mn^{2+}, Mg^{2+} and other cations that exist on the surface of BC/PAL that will conduct ion exchange with Cd^{2+} and Pb^{2+} to reduce the bioavailability of harmful heavy metals in soil (Dai et al., 2017). In addition, anions such as CO_3^{2-}, OH^-, SO_4^{2-}, PO_4^{3-} released from BC/PAL can also combine with heavy metals to form insoluble precipitates. For example, BC/PAL contains PO_4^{3-}, which can reduce the mobility of Pb^{2+} in soil by forming the precipitation of insoluble Pb-phosphate (Beesley et al., 2011). The general reaction formula is expressed as follows (M is heavy metals):

$$(\text{BC/PAL-O})_2\text{Mg}+\text{M}^{2+}\rightarrow(\text{BC/PAL-O})_2\text{M}+\text{Mg}^{2+} \tag{Eq.3}$$

(Ion exchange with surface salt base ions, taking Mg^{2+} as an example)

$$\text{BC/PAL-PO}_4^{3-}+\text{M}^{2+}\rightarrow\text{BC/PAL-M}_3(\text{PO}_4)_2 \tag{Eq.4}$$

(Precipitation with mineral components, taking PO_4^{3-} as an example)

Fractions of Cd and Pb

The major change in Cd and Pb chemical fractionations indicated that biochar-palygorskite composites transform the Cd and Pb from active speciation to stable speciation, thereby reducing the bioavailability and ecotoxicity of heavy metals in the environment. It may because the OH- distributed on the surface of BC/PAL increases the pH value of the soil, and the Cd and Pb in the soil are precipitated in the form of

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insoluble salts such as hydroxide, which affects the speciation transformation and distribution of Cd and Pb in the soil. A large amount of hydroxyl functional groups can be complex with heavy metals in the soil, causing changes in the reducible content of Cd and Pb in soil (Xu et al., 2020b). As we all know, the change of pH value will also affect the content and mobility of available heavy metals in soil. The elevate of soil pH increases the number of negative charges in the soil, and the negative charges form complexation with heavy metal ions to form precipitation, which converts the available state of heavy metals to other speciations, thereby reducing the availability of Cd and Pb in the contaminated soil.

Contents of Cd and Pb in corn

Compared to the untreated sample, biochar-palygorskite composite significantly reduced the Cd and Pb accumulations in both shoot and root parts of corn, and the effects were more pronounced by the high mass ratio of palygorskite. In reducing the accumulation of heavy metals in corn, adding PAL or BC alone also has a certain effect, but the effect is not as significant as adding the biochar-palygorskite composite.

Because of the increase in soil pH, the change of soil structure, and the reduction of the bioavailability of heavy metals, the growth of corn and the accumulation of Cd and Pb were effectively promoted after the soil was remediated by the biochar-palygorskite composite. This further confirmed that BC/PAL could improve the soil quality and reduce the ecotoxicity of soil contaminated by heavy metals.

Conclusion

Stabilization of biochar-palygorskite composite as a stabilizer is a sophisticated stimulation technique to treat the Cd and Pb contaminated soil. Remediation with composites transformed the active speciation of Cd and Pb to stable speciation, and decreased the $CaCl_2$-extracted Cd and Pb concentrations in the soil. Appling the biochar-palygorskite composite can improve the soil enzyme activity and illustrated that the soil metabolism was enhanced effectively. At the same time, treatment with composites increased the soil pH, available nutrient contents and organic carbon content significantly. The improvement of soil physical and chemical properties and the decline of Cd and Pb bioavailability significantly thus promoted the growth of corn and reduced the accumulation of heavy metals in various parts. In conclusion, the biochar-palygorskite composite was an efficient, environmentally friendly and cheap Cd and Pb soil remediation material, which can improve the soil conditions and increase crop yields in field applications.

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